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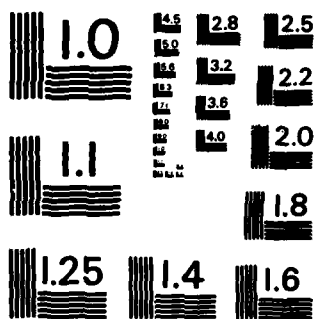
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Poly(3,6-N-methylcarbazolyl methylene) prepared by acid-catalyzed condensation polymerization of N-methylcarbazole with formaldehyde exhibits p-type semiconducting properties when doped with electron acceptors such as iodine, bromine, nitrosyl tetrafluoroborate, and nitrosyl hexafluoroantimonate. The polymer samples have T_g in the range 100-148°C, chain length in the range 13-25, and molecular weight distribution of 1.17-1.51. The polymer complexes with dopant anion (I_3^- , Br_3^- , BF_4^-) to polymer repeating unit ratio of 0.67-0.95 have d.c. conductivity of 10^{-3} to 10^{-1} ohm⁻¹/cm and a positive thermoelectric voltage at 23°C.

An important new feature of the methylene-bridged polycarbazole conducting polymers is doping-induced polymer backbone conjugation of the form $-CH_2- \rightarrow =CH-$. Evidence for this oxidation mechanism, converting methylene linkages to methine linkages, includes elemental analysis, infrared spectra, proton NMR, and electron spin resonance results.

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ELECTRICALLY CONDUCTING COMPLEXES OF
POLY(3,6-N-METHYLCARBAZOLYL METHYLENE)*

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Abstract

Poly(3,6-N-methylcarbazolyl methylene) prepared by acid-catalyzed condensation polymerization of N-methylcarbazole with formaldehyde exhibits p-type semiconducting properties when doped with electron acceptors such as iodine, bromine, nitrosyl tetrafluoroborate, and nitrosyl hexafluoroantimonate. The polymer samples have T_g in the range 100-148°C, chain length in the range 13-25, and molecular weight distribution of 1.17-1.51. The polymer complexes with dopant anion (I_3^- , Br_3^- , BF_4^-) to polymer repeating unit ratio of 0.67-0.95 have d.c. conductivity of 10^{-3} to $10^{-1} \text{ ohm}^{-1} \text{ cm}^{-1}$ and a positive thermoelectric voltage at 23°C.

An important new feature of the methylene-bridged polycarbazole conducting polymers is doping-induced polymer backbone conjugation of the form $-CH_2- \rightarrow =CH-$. Evidence for this oxidation mechanism, converting methylene linkages to methine linkages, includes elemental analysis, infrared spectra, proton NMR, and electron spin resonance results.

* Presented in part at the Symposium on Chemistry of Conductive Polymers, 188th ACS National Meeting, Philadelphia, August 26-31, 1984.

INTRODUCTION

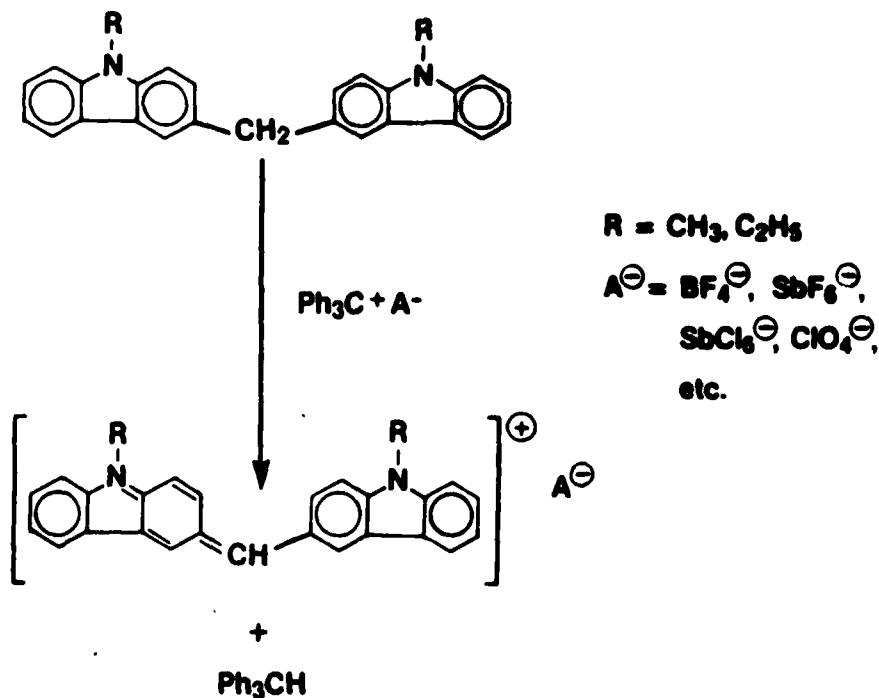
Electrically conducting organic polymers are currently of great scientific interest for both theoretical and practical reasons. Highlights of progress made to date and discussions of the major unsolved problems in currently known conducting polymers are covered in recent review papers [1-5]. As electronic materials, the most promising synthetic semiconductors and metals for practical electronic applications are those which can combine solution or melt processibility to thin films, environmental stability and good mechanical properties with high conductivity. None of the widely known polymers has yet shown this combination of desired properties [1-5].

We recently reported the preparation and properties of poly(3,6-N-methylcarbazolyl) (PMCZ) which is highly conducting when doped with iodine, air stable, and soluble in a number of organic solvents including nitrobenzene [6-7]. Unfortunately, the polymer became insoluble in the THF solvent used for the Grignard coupling polymerization at $DP \sim 10$. The glassy PMCZ films cast from a nitrobenzene solution consisted of oligomers with $DP = 2-13$ and were consequently brittle. The rigid biaryl linkage would not be expected to give rise to a sub T_g backbone relaxation usually necessary for ductility in the glassy state [8-9]. Significant improvement in the mechanical properties of PMCZ was achieved at high iodine doping levels through plasticization by the anions, large increase in the molecular weight, and some crosslinking induced by radical cation coupling. In fact, PMCZ polymers synthesized by a one-step simultaneous polymerization and doping in solution and films cast from the liquid iodine solvent exhibited good flexibility and mechanical strength [10].

One obvious way to improve mechanical strength, solubility, and processibility is to introduce flexible bridging groups between the rigid aromatic sections. For example, polyphenylene oxides, sulfides, and methylenes, $\{Ar-X\}_n$, $X = O, S, CH_2$, have all been polymerized to high molecular weight materials which are

soluble and form ductile glasses of high strength. Upon complexing, however, the bridging group orbitals must be able to hybridize and overlap with the π system of the adjacent aromatic groups in order to achieve high conductivity. Thus, only complexes of $\{\text{Ar-S}\}_n$ are highly conducting because of the greater ability of sulfur to rehybridize [11]. Ring fusion to planar benzothiophene structure also assists charge mobility in polyphenylene sulfide at high degrees of complexing [4]. Unfortunately, an excessive amount of crosslinking also occurs under these conditions and the complex embrittles. Also, complexes of polyphenylene derivatives are environmentally unstable.

Our strategy to introduce bridging flexible units, such as $-\text{CH}_2-$, into polycarbazole backbone to improve mechanical properties was further encouraged by the fact that stable salts of bis-(9-alkyl-3-dicarbazolyl) methyl cation have previously been prepared. Bruck *et al* [12] and Nishide *et al* [13] have shown that a hydrogen of the bridge methylene of bis(9-alkyl-3-dicarbazolyl) methylene can be abstracted as a hydride ion by reagents such as triphenylmethyl tetrafluoroborate ($\text{Ph}_3\text{C}^+\text{BF}_4^-$), triphenylmethyl perchlorate ($\text{Ph}_3\text{C}^+\text{ClO}_4^-$) and triphenylmethyl hexachloroantimonate ($\text{Ph}_3\text{C}^+\text{SbCl}_6^-$) to form the salt of highly conjugated imine cations shown below:



It may be expected that the cation of the methylene-bridged polycarbazole would be delocalized in both carbazoyl rings facilitating charge transport and cation stability.

In this paper we describe the synthesis and characterization of poly(3,6-N-methylcarbazoyl methylene) (PMCZM) and its acceptor-doped complexes with the objective of elucidating the charge transport mechanism.

EXPERIMENTAL

Polymer Synthesis

The preparation of PMCZM was achieved by acid-catalyzed condensation polymerization of N-methylcarbazole with formaldehyde [14-16]. Four samples of PMCZM were prepared in four polymerizations as described below: 1) A solution of 1.8124g(0.01 mole) N-methylcarbazole and 0.01 mole formaldehyde (0.811g of 37% aqueous solution) in 15 ml dioxane containing 0.184 ml conc. H_2SO_4 ($d=1.84g/cm^3$) was sealed in a 1 inch dia x 5 inch long pyrex glass tube. The reaction vessel was heated in an oil bath at $90^\circ C$ for 3 hours with continual shaking. Then the reaction mixture was poured into 1.0 liter of well-stirred methanol to precipitate the polymer. The precipitate was dissolved in N-methyl-2-pyrrolidone (NMP) and re-precipitated in methanol to produce a white polymer. 2) The same procedure as in 1) was used except that 5.4337g(0.03 mole) N-methylcarbazole, 2.433g(0.03 mole) 37% formaldehyde solution, 0.55 ml conc. H_2SO_4 , and 45 ml dioxane was used. 3) A reaction mixture of 18.124g(0.10 mole) N-methylcarbazole, 8.11g 37% formaldehyde, 1.84 ml conc. H_2SO_4 , and 150.0 ml dioxane was prepared in a 500 ml 3-neck flask in flowing argon atmosphere (2 ml/min.). After mechanically stirring at $86^\circ C$ for 3 hours, the reactor mixture was poured into 3.0 liters of rapidly stirring methanol to precipitate the polymer. The polymer was twice dissolved in 250 ml NMP and precipitated in methanol, giving a white product. 4) The same procedure as 1) was used except that 0.3003g(0.01 mole) of paraformaldehyde $(CH_2O)_x$, was used in place of the formaldehyde solution.

Characterization of Undoped and Doped Polymers

Polymer molecular weight distribution was characterized using a Waters Associate Model 501 Gel Permeation Chromatography (GPC) at room temperature (23°C). The GPC was packed with 10^5 , 10^4 , 10^3 , and 500Å microstyrogel columns in methylene chloride solvent and operated at a flow rate of 2 ml/min. The infrared spectra of thin polymer films cast from methylene chloride solutions were recorded on KCl windows or as free standing films using a Digilab model FTS-14 Fourier transform spectrometer. A Cary 17 spectrophotometer was used to obtain the spectra of thin polymer films cast on NaCl plates in the 300-3000 nm region. These films were oxidized on the substrates by exposing them either to I_2 vapor or a hexane solution of I_2 at 50°C, or a solution of $NOBF_4$ (Aldrich) in acetonitrile at 25°C under nitrogen atmosphere.

Electron Spin Resonance (ESR or EPR) studies were done using a Varian E-4 EPR spectrometer and either solid powdered samples or dilute nitrobenzene solutions at 25°C. The first derivative of the ESR spectrum of the polymer complexes was numerically double integrated and compared with a known concentration of the standard 1,1-diphenyl picrylhydrozyl diluted with N-methylcarbazole or dissolved in nitrobenzene in order to calculate the spin concentration. Quartz tubes of 3.175mm O.D. were used instead of the usual tubes in order to avoid possible swamping of the ESR signal by an excessive amount of the high dielectric constant nitrobenzene. The proton NMR spectra of doped PMCZM samples were obtained at room temperature (25°C) using a NT-300 NMR spectrometer. The BF_4^- -doped PMCZM samples for NMR analysis were prepared by mixing separate nitrobenzene solutions of polymer and $NOBF_4$ in a ratio of one $NOBF_4$ per polymer repeat unit. Upon mixing of the two solutions the color turned dark blue, indicating formation of the charge transfer complex.

Electrical conductivity measurements were made on complexed films at room temperature (23°C) with a standard four-point probe

instrument and a contactless conductivity instrument (Tencor M-gage) operating at 1kHz. Halogen-doped PMCZM films for electrical conductivity measurements were prepared by vapor phase doping of polymer films deposited on glass slides. Thermal Analysis (DSC and TGA) was done using a DuPont 1090 instrument in nitrogen or air.

RESULTS AND DISCUSSION

Physical Properties of Undoped and Doped Polymers

The PMCZM samples were considerably more soluble and in more solvents than PMCZ, as expected. In addition to nitrobenzene, which is a good solvent for PMCZ, the methylene bridged polymer samples were also soluble in N-methyl-2-pyrrolidone (NMP), methylene chloride, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), and similar solvents. The molecular weight distribution of the PMCZM samples obtained by GPC analysis is shown in Figure 1. The molecular weight parameters calculated using polystyrene standards are collected together in Table 1. The narrow molecular weight distribution (M_w/M_n) of 1.17-1.51 in the four polymer samples is to be noted. Usually at very high conversions, step-growth (condensation) polymerizations give polymers with M_w/M_n close to 2.0 [17]. The effect of polymerization conditions on M_w/M_n is not very significant; however, a significant variance between 13-25 is observed in the number-average degree of polymerization DP.

Differential scanning calorimetry (DSC) analysis of the PMCZM samples showed a glass transition temperature (T_g) in the range of 100-148°C, T_g increasing with increasing molecular weight. A typical DSC thermogram of a PMCZM sample is shown in Figure 2. The absence of any endothermic peaks in the DSC thermograms up to 300°C together with the well-defined T_g indicated that the polymer samples were largely amorphous. Figure 3 shows the thermal stability of a PMCZM sample in nitrogen atmosphere, indicating onset of decomposition at about 400°C.

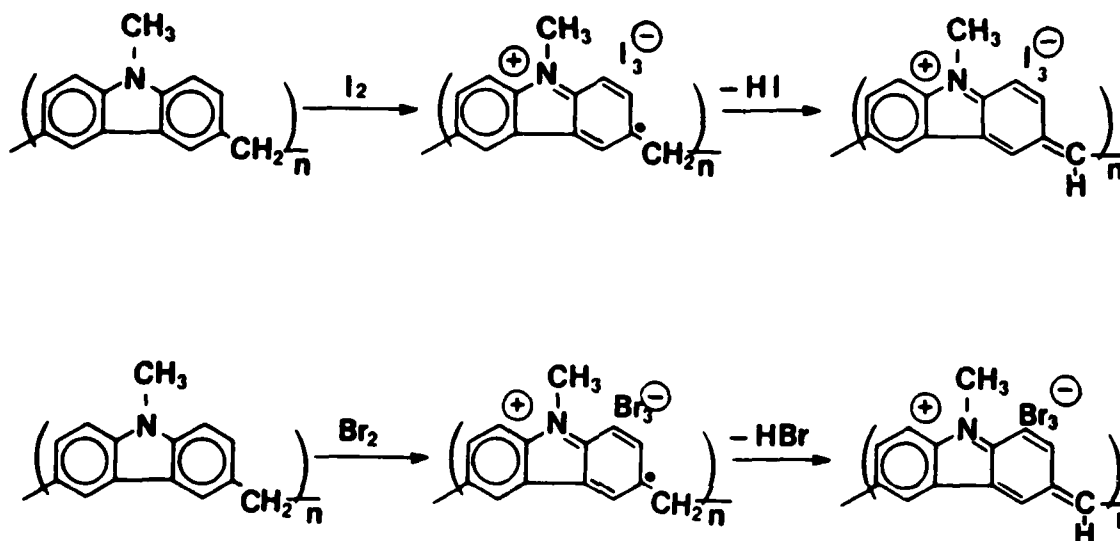
The d.c. conductivity of iodine-doped PMCZM samples at 23°C was about 10^{-3} to 10^{-2} $\text{ohm}^{-1}\text{cm}^{-1}$ as shown in Table 1. Bromine-doped samples of PMCZM have higher d.c. conductivity, about $0.1 \text{ ohm}^{-1}\text{cm}^{-1}$. NOBF_4 and NOSbF_6 also dope PMCZM films in acetonitrile solutions to high conductivity; however, the electrical properties have not yet been fully characterized. Thermoelectric voltage measurements on iodine- and bromine-doped PMCZM films gave +5.4 mV and +3.8 mV, respectively, indicating that the doped polymer complexes were p-type materials.

The effect of molecular weight or degree of polymerization on electrical conductivity is not yet clear from the chain length of about 13-25 achieved so far, although it appears that the polymer with the longest chain length has the highest conductivity. From studies of p-phenylene oligomers and polymers [13] and polyacetylene samples with M_n from 400-870,000 [19-20], it has recently been suggested that the chain length, beyond a certain minimum, may only be of minor relevance to electrical conductivity. Evidently in the aromatic polymers, the principal charge transport mechanism is intermolecular, along stacks of face to face packed aromatic rings. Delocalization of carriers along the chain serves mainly to increase the probability of hopping between chains. Beyond a certain conjugation length, one might expect this probability to be unchanged. The minimum chain length required to give the maximum conductivity in a doped polymer can be expected to vary somewhat from one polymer backbone structure (repeating unit) to another.

Figure 4 shows the UV-Visible-Near IR spectra of undoped and NOBF_4 and iodine-doped PMCZM films. Two new absorbance peaks are observed upon doping. The absorbance at 700 nm wavelength is attributed to the intrachain dication transitions and that at 1300 nm to intermolecular hopping. Observation of the 700nm transition in both NOBF_4 and iodine-doped samples clearly rules out the possibility of polyiodides as its origin. Also, the concentration behavior and the long wavelength nature of the 1300nm absorption band suggest an intermolecular charge transfer process, most probably between neutral and charged sections of the polymer chains similar to our model compound results [7].

Doping-Induced Polymer Backbone Conjugation

The oxidation of PMCZM is expected to proceed by the following mechanism in which an intermediate radical cation is generated but subsequently decomposed with release of a methylene bridge hydrogen and formation of a stable cation similar to the previously cited results for the dimer:



The observed fairly high d.c. conductivity of PMCZM complexes is consistent with doping-induced polymer backbone conjugation which presumably facilitated intrachain contribution to p-type conductivity. The 10^{-3} to 10^{-2} ohm⁻¹ cm⁻¹ room temperature conductivity of iodine complexes of PMCZM is to be compared to 1-10 ohm⁻¹ cm⁻¹ typically observed in the iodine complexes of the parent unbridged polycarbazoles [6-7,10]. Conceivably, the orders of magnitude lower conductivity of PMCZM compared to PMCZ is due to a significant number of methylene linkages not converted to methine linkages in the doped polymer. Indeed, the composition of PMCZM complexes shows that the mole ratio (γ) of dopant counterion to polymer repeating unit containing methylene linkages is less than 1, Table 2. The composition results of

Table 2 also show that bromine doping gives the highest conductivity ($0.1 \text{ ohm}^{-1} \text{ cm}^{-1}$) and correspondingly the highest doping level, $y = 0.95$.

Further evidence for the proposed oxidation mechanism was sought using a multitude of techniques: ESR, proton NMR, IR of doped and undoped polymer films, and direct IR observation of the gaseous products of halogen doping (HBr, HI).

ESR analysis shows a very low spin concentration of 2.3×10^{-3} /polymer repeating unit in the solid state PMCZM-iodine complex and 7.4×10^{-4} /polymer repeating unit in dilute (0.01 g/ml) nitrobenzene solution of PMCZM-iodine complex. No change in spin concentration with time was observed. The difference between spin concentrations in solution and the solid state is considered to be within experimental error. A g value of 2.0039 ± 0.0009 and 2.0024 ± 0.0009 was found for the unpaired electrons in the solid samples and dilute solutions, respectively. The observed ESR signal in both solid and solution samples was a broad symmetric line, $\Delta H_{1/2} = 15\text{G}$.

Assuming that all the iodine uptake upon doping can be associated with I_3^- counterions, approximately 67-83% of the polymer repeating units should be radical cations. As suspected, the significantly lower spin concentration suggests that the radical cations generated during doping decompose to cations by loss of a hydrogen atom at the bridge carbon. An alternative interpretation of the very low spin concentration in the case of the solution results, for example, radical cation exchange interaction to produce a single diamagnetic state which does not contribute to the ESR signal, was ruled out in view of our prior model compound studies which showed that this does not occur in dilute solutions [7].

Elemental analysis (Galbraith Laboratories, Inc.) gave the following results. Undoped PMCZM: %C = 86.61; %H = 5.87; %N = 7.01. Iodine-doped PMCZM: %C = 56.77; %H = 3.59; %N = 4.62; %I = 34.78. It should be noted that the ratio of

hydrogen to carbon found decreases from 0.068 to 0.063 upon doping. If dehydrogenation does not occur upon doping, the H/C ratio will not decrease. However, if the methylene linkages of PMCZM were completely converted to methine linkages upon doping, the theoretical H/C ratio will decrease from 0.066 to 0.060. Elemental analyses of other samples at different levels of doping always showed a decrease in the H/C ratio upon doping. Therefore, we conclude that the overall process in acceptor-doping of PMCZM is essentially a dehydrogenation reaction of the form: $-\text{CH}_2- \rightarrow =\text{CH}-$. Halogenation reactions and halogen-substitution products, as part of the halogen-doping process, for example $-\text{CH}- \rightarrow =\text{CX}-$ or $-\text{CH}_2 \rightarrow -\text{CHX}-$ (where $\text{X} = \text{Br}, \text{I}, \text{or Cl}$), are considered unlikely. This is in view of the p-type nature of the electrical conductivity implying a significant intrachain contribution to charge transport, the fact that NOBF_4 and NOSbF_6 also dope PMCZM, and the infrared and proton NMR results discussed below.

The FTIR spectra of PMCZM and iodine-doped PMCZM thin film samples are shown in Figure 5. The spectrum of the undoped PMCZM (Figure 5,A) confirmed the polymer structure, showing the characteristic 3,6-carbazolyl absorption band at 800 cm^{-1} (1,2,4-trisubstituted benzene rings), methylene scissoring at 1490 cm^{-1} and methylene bending at 1430 cm^{-1} . The expected aromatic and aliphatic CH stretching vibration bands in the $2800\text{--}3100 \text{ cm}^{-1}$ region were also observed. The spectra of the same PMCZM film after its exposure to iodine vapor for 10 sec and 5 min are shown at B and C respectively, Figure 5. There are considerable changes in the infrared spectrum of PMCZM after doping. A significant decrease in the intensity of the methylene absorption bands ($1430, 1490, \text{ and } 2930 \text{ cm}^{-1}$) is observed in the complexed PMCZM films. Also, in comparing spectrum C to A in Figure 5, we see a significant intensification and shift of the positions of several bands ($1060, 1115, 1325, 1375, 1590 \text{ cm}^{-1}$) and appearance of new bands ($1510, 1565 \text{ cm}^{-1}$). These results are in accord with the expected loss of a methylene hydrogen in the polymer backbone upon doping, resulting in a methine-bridged conjugated polymer backbone. The lack of any new infrared absorption bands

characteristic of carbon-halogen bonds in the $500\text{--}650\text{ cm}^{-1}$ region rules out halogenation upon halogen-doping.

Direct observation of the gas evolved during halogen doping of PMCZM was made using an infrared gas cell of 12.70 cm path length previously described [10]. Figure 6 shows the FTIR spectrum of the gas evolved during bromine doping of PMCZM. HBr gas with absorption bands in the $2400\text{--}2800\text{ cm}^{-1}$ region is clearly identified. Some bands at $2300\text{--}2400\text{ cm}^{-1}$ and $2800\text{--}3200\text{ cm}^{-1}$ also present in the spectrum have been established as artifacts due to the glue used to attach KCl windows to the gas cell. HI gas similarly evolved during iodine doping could not be detected with IR using the same gas cell; a gas cell of approximately 25 cm path length would be required. Nevertheless the halogen doping results confirm the proposed oxidation mechanism.

Figure 7 shows the proton NMR spectra of undoped and NOBF_4 -doped PMCZM. Assignment of peaks was based on the integrals of peaks and comparison with the NMR spectrum of the dimer. The expected number of aromatic and N-methyl protons, 6 and 3 respectively, were obtained in both the doped and undoped samples to within experimental error. The expected 2 methylene protons at the bridge carbon in undoped PMCZM was also obtained. However, only 1.2 protons at the bridge carbon were found in NOBF_4 -doped PMCZM. This clearly shows that the overall doping process is a dehydrogenation reaction in accord with the other experimental results. Also, we note that although one BF_4^- to one polymer repeating unit was mixed in solution, the indicated ratio from the protons found in the PMCZM complex is less than 1.

CONCLUSION

We have prepared electrically conducting complexes of poly(3,6-N-methylcarbazolyl methylene) (PMCZM) which have p-type conductivity in the range 10^{-3} to $10^{-1}\text{ ohm}^{-1}\text{ cm}^{-1}$ at room temperature (23°C) using iodine, bromine, nitrosyl tetrafluoroborate, nitrosyl hexafluoroantimonate and other acceptor dopants. The polymers prepared by acid-catalyzed

condensation polymerization of N-methyl-carbazole with formaldehyde have average chain lengths from 13-25 and were largely amorphous with glass transition temperature from 100-148°C. Even higher molecular weight materials should be obtainable by optimization of the polymerization process.

An important new feature of the conducting complexes of PMCZM is doping-induced polymer backbone conjugation in which the methylene linkages are converted to methine linkages:

$-\text{CH}_2- \rightarrow =\text{CH}-$. Evidence for this oxidation mechanism was provided by elemental analysis, infrared spectra, proton NMR, ESR, and thermoelectric voltage results.

ACKNOWLEDGEMENTS

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Table 1. Properties of Poly(3,6-N-methylcarbazolyl Methylene) Samples and d.c. Conductivity of Iodine-Doped Samples.

PMCZM Samples	M_w	M_n	M_w/M_n	DP	$T_g(^{\circ}\text{C})$	$(\Omega^{-1}\text{cm}^{-1})$
1	2931	2497	1.17	12.9	100	10^{-3}
2	4090	3221	1.27	16.7	111	10^{-3}
3	7194	4767	1.51	24.7	148	10^{-2}
4	2943	2457	1.20	12.7	101	10^{-3}

Table 2. Composition of PMCZM Complexes Where y is the Molar Ratio of Dopant Counterion to Polymer Repeating Unit.

Dopant Counterion	y	(ohm ⁻¹ cm ⁻¹)
I_3^-	0.67 ^a -0.83 ^b	10 ⁻³ to 10 ⁻²
Br_3^-	0.95 ^b	0.1
BF_4^-	0.75 ^b -0.80 ^c	---
SbF_6^-	---	---

a - elemental analysis
 b - weight uptake
 c - NMR

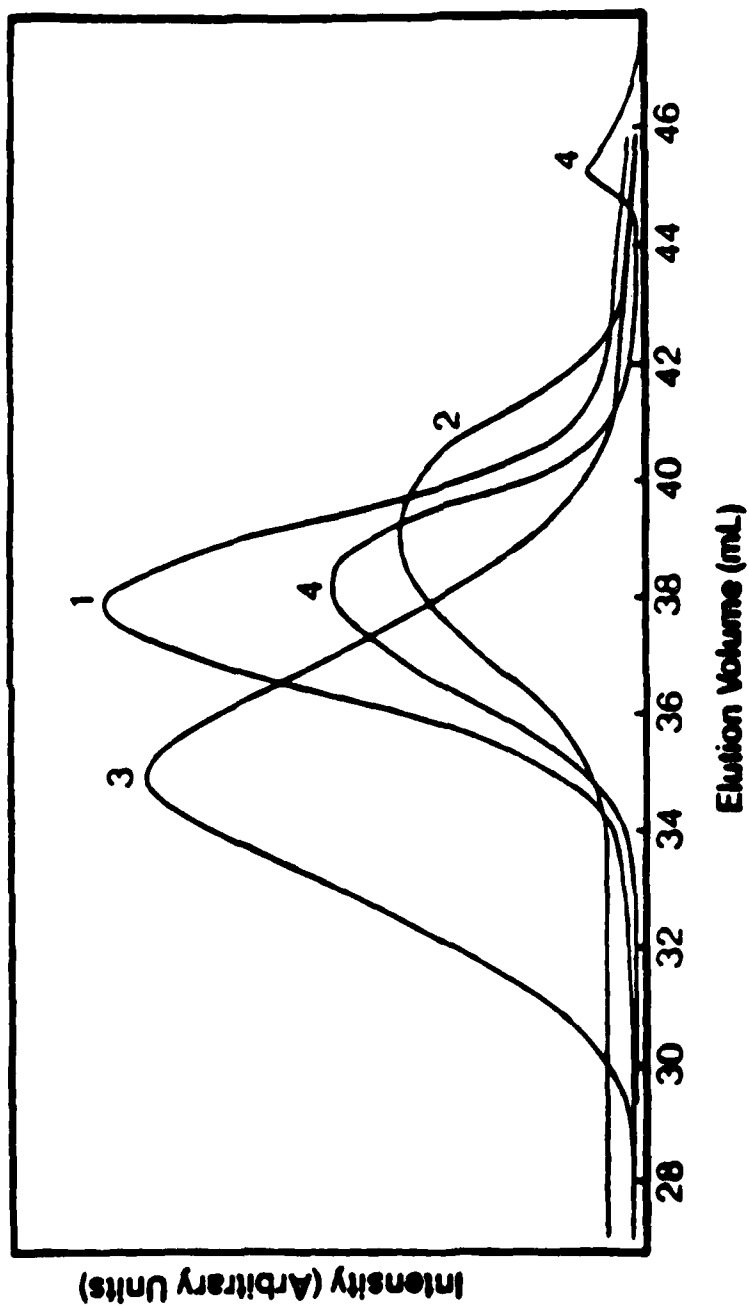


Figure 1. Molecular weight distributions of PMCZM in four polymerizations.

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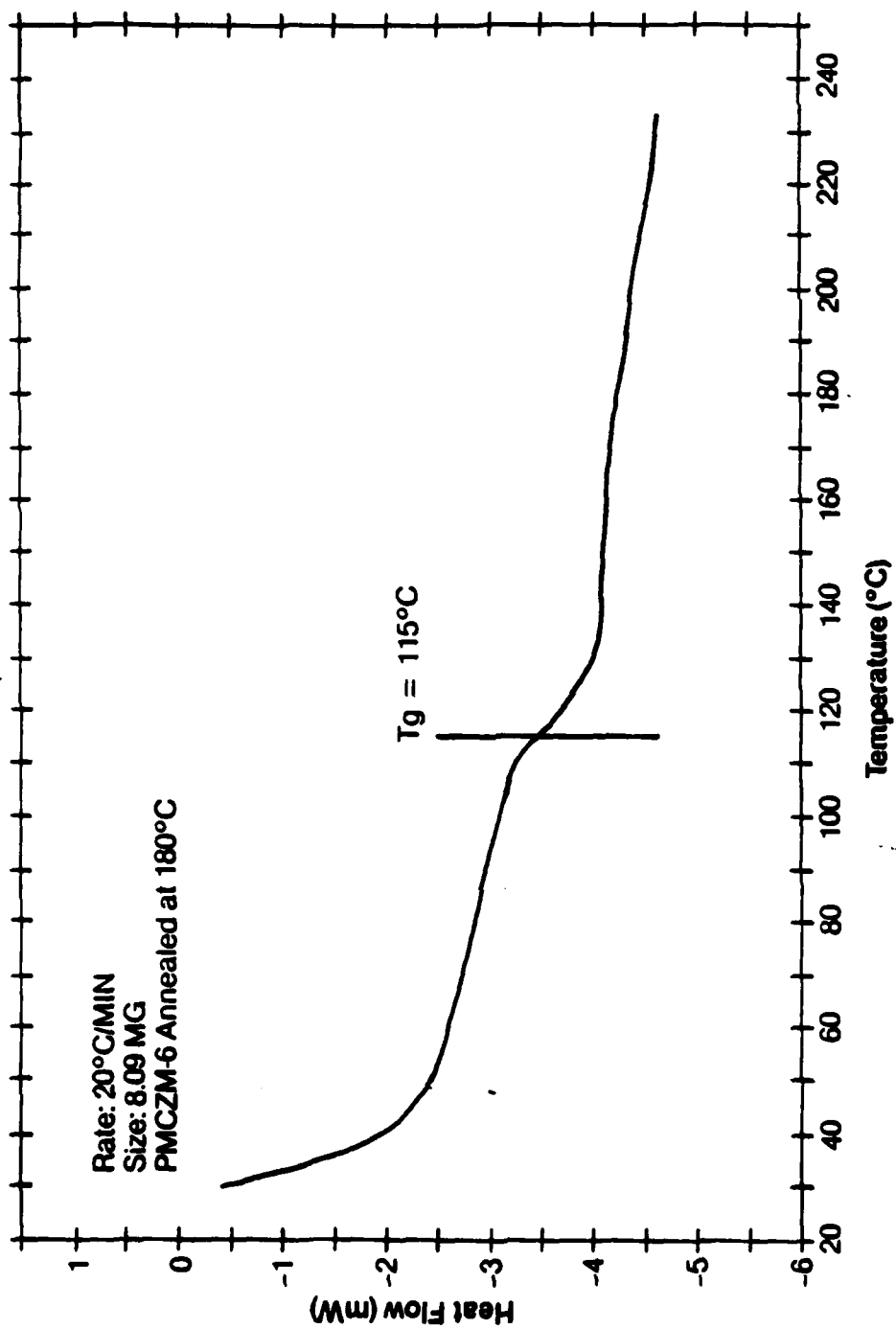


Figure 2. DSC thermogram of a PMCZH sample.

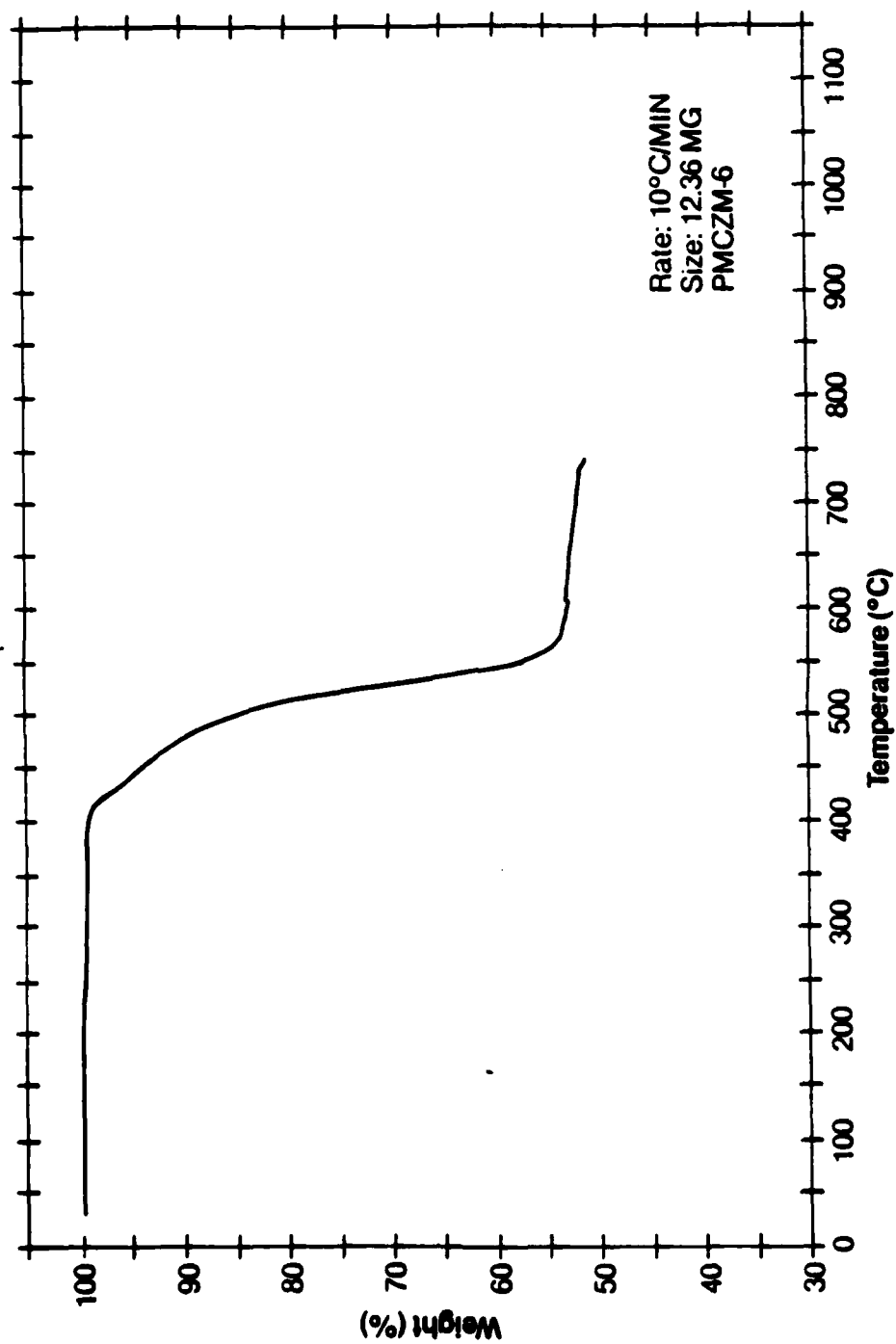


Figure 3. Thermogravimetric weight loss curve of a PMCZM sample.

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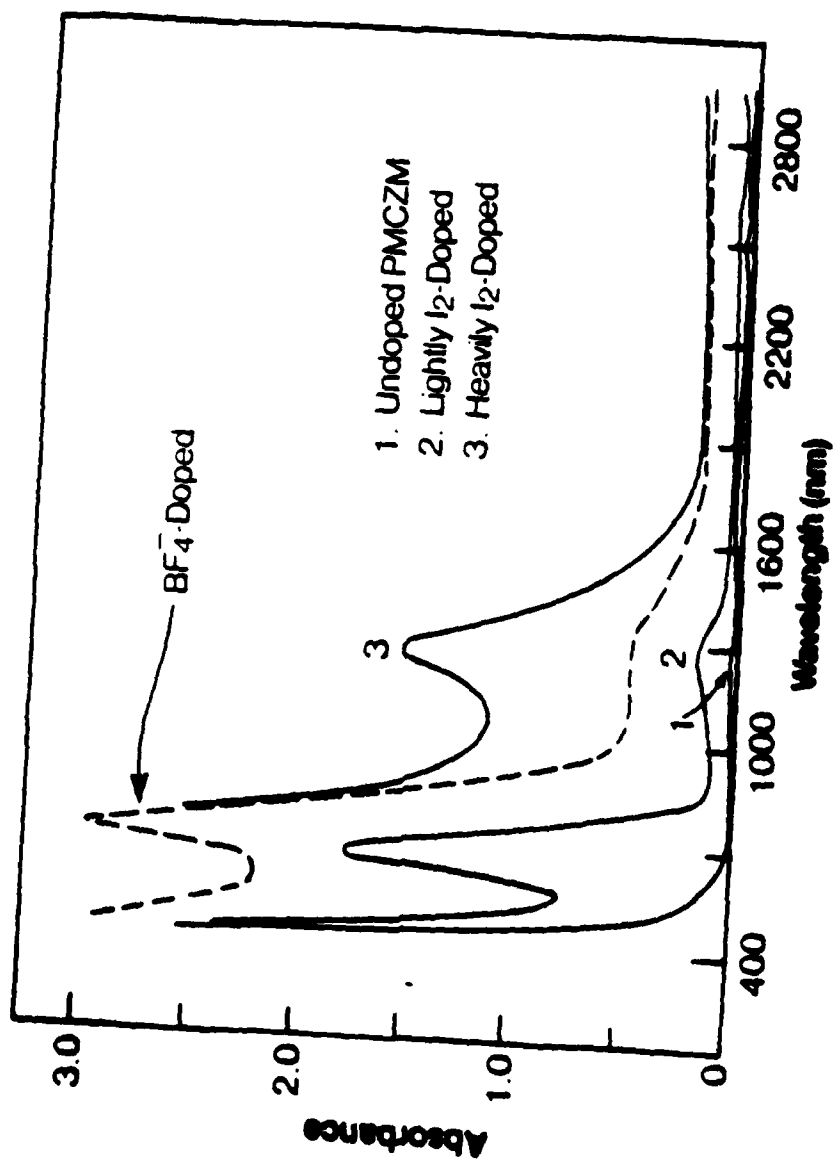


Figure 4. UV-Visible-Near IR spectra of undoped and iodine- and BF₄⁻-doped PMCZM films.

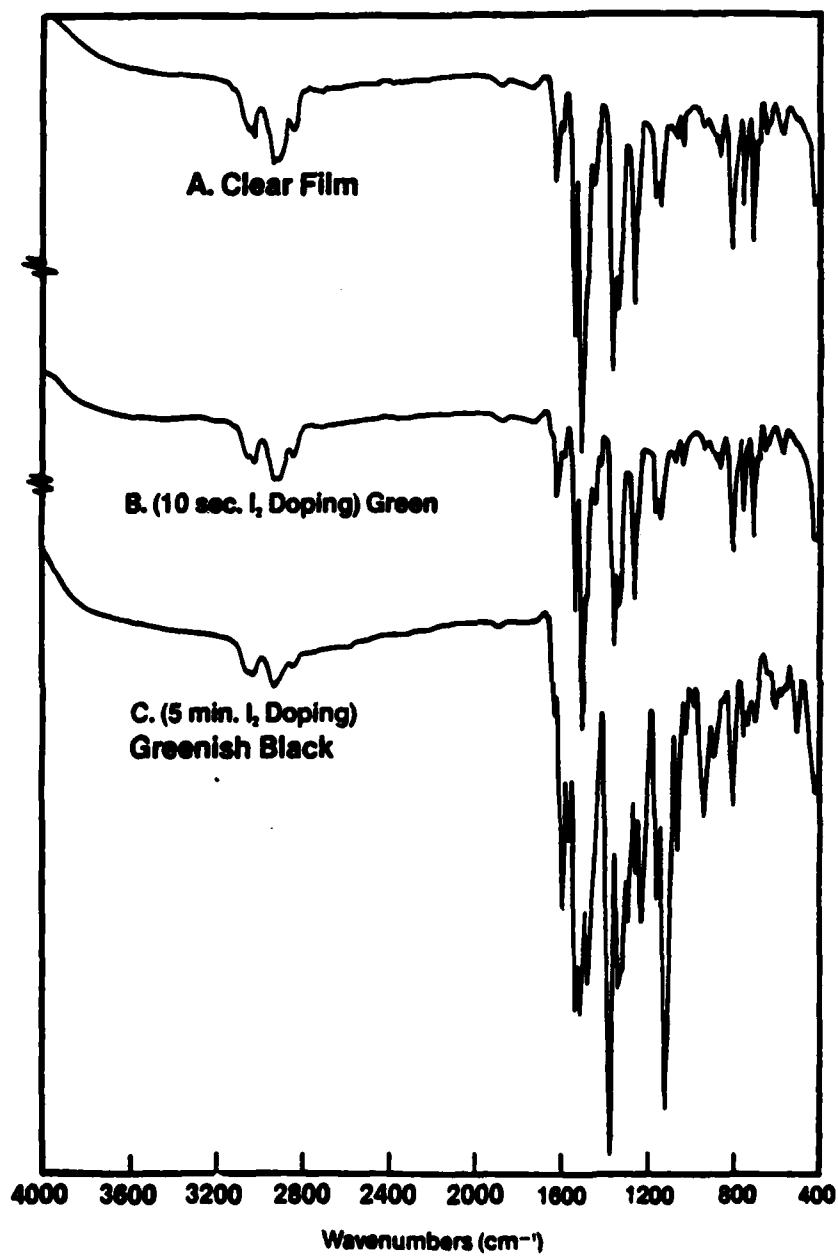


Figure 5. Fourier Transform infrared spectra of: A - undoped PMCZM film; B - iodine-doped green PMCZM film; C - further iodine-doped greenish black PMCZM film.

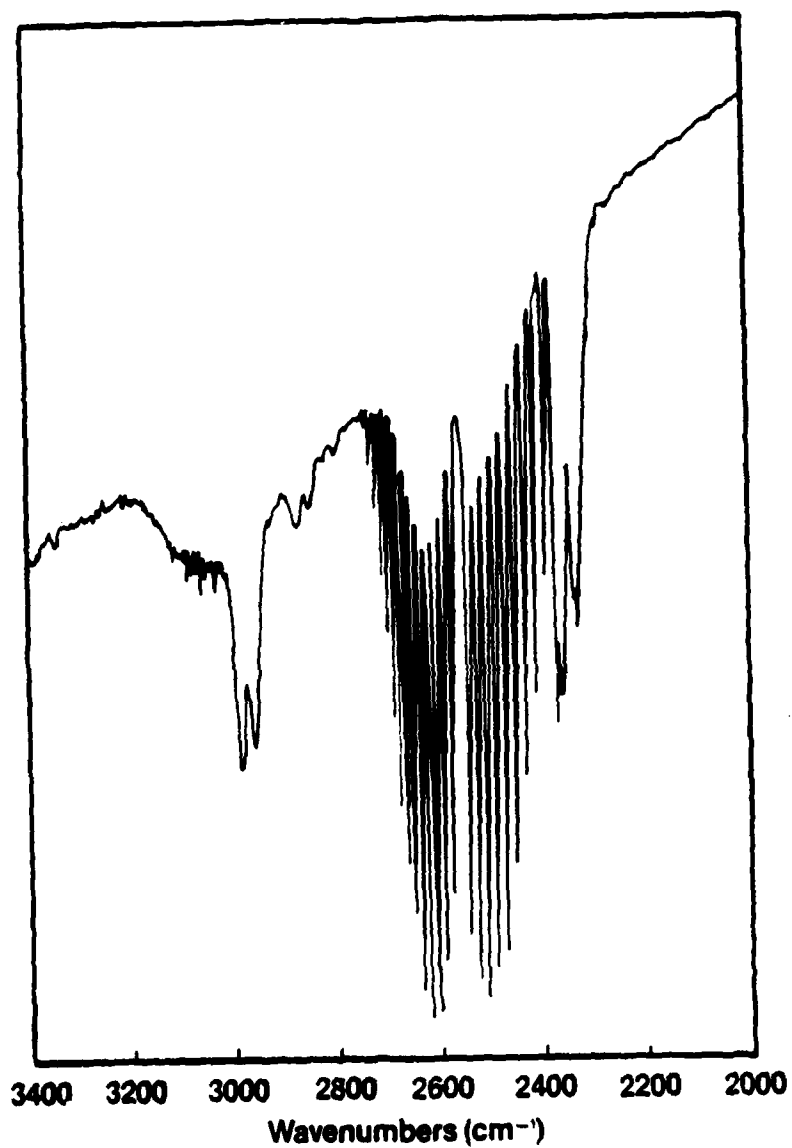


Figure 6. Fourier Transform infrared spectrum of gas evolved during bromine doping of PMCZM.

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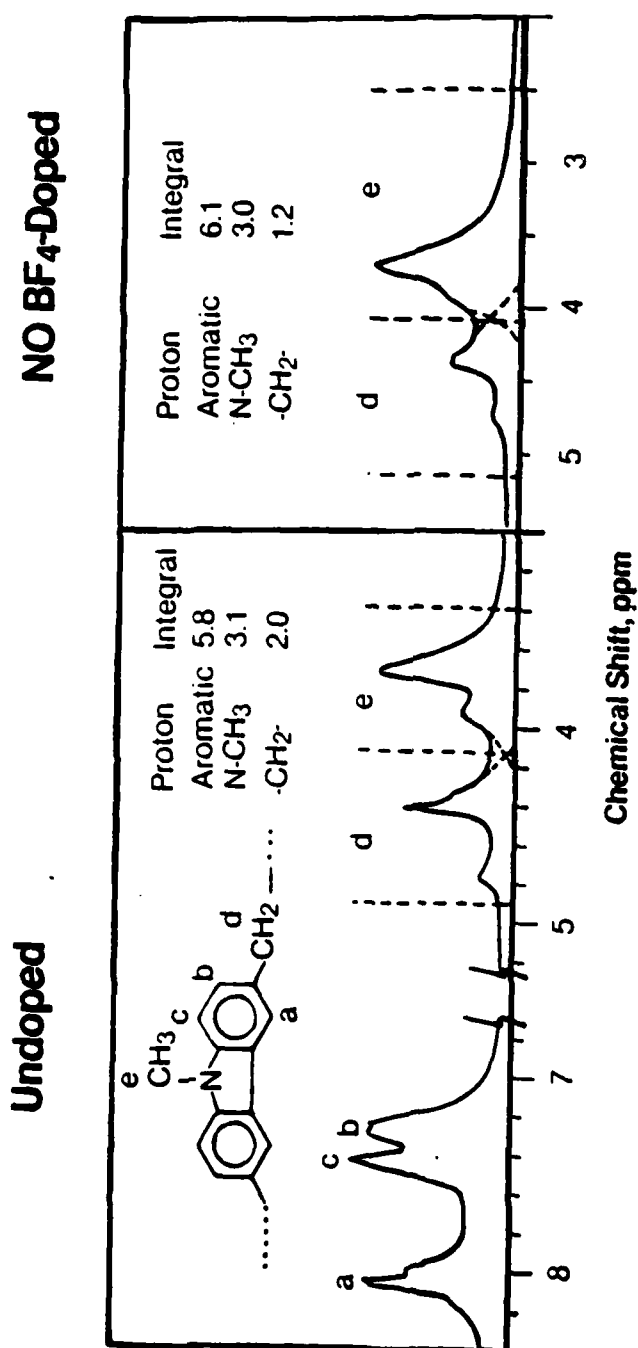


Figure 7. Proton NMR spectra of undoped and NOBF₄-doped PMCZM films.

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